

DETERMINATION OF CERTAIN OUTER X-RAY ENERGY LEVELS FOR
THE ELEMENTS FROM ANTIMONY (51) TO SAMARIUM (62)

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the
degree of Doctor of Science in the University of Michigan.

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ABSTRACT

X-ray L absorption edges and corresponding emission lines for elements Sb(51) to Sa(62).—The three L absorption edges and certain adjacent emission lines of the same element were photographed for series of ten elements from antimony to samarium. Thus a direct measurement of the distances on the photographic plates from the $L\beta_2$ line to the L_{III} edge, from $L\gamma_1$ to L_{II} , and from $L\gamma_4$ to L_I made possible the determination of the N_{IV} , N_V , and O_{II-III} energy levels respectively. In certain cases the edge and line were obtained on separate plates having the same reference line. The method seems to be an advantageous one in cases in which the energy of the desired level is so small that a slight error in the wave-length of either absorption edge or emission line would make a considerable error when computations are based upon determinations of these by different investigators. Particulars are given concerning the making of *absorbing screens containing free antimony, tellurium and iodine*. With these screens the L_I absorption edges for Sb(51), Te(52), and I(53) were found at 2631.7, 2503.9 and 2383.9 x-units; L_{II} edges at 2821.9, 2679.3 and 2547.5 x-units; and L_{III} edges at 2990.7, 2845.7 and 2713.9 x-units, respectively.

Variation with atomic number of the values of the N_{IV} , N_V and O_{II-III} energy levels.—The N_{IV} and N_V levels, which form a relativity doublet, are very close together in the case of the lower elements studied and show a slightly greater separation for the higher elements. All the curves showing the variation of energy level with atomic number show a distinct bend at lanthanum (57) as is to be expected according to the existing theory, for the next element, cerium, marks the beginning of the rare earth group. The O_{II-III} curve for antimony, tellurium and iodine runs nearly horizontal, and as this level represents the outermost occupied orbit in these elements, the values obtained should be related to the ionizing potential. The values so computed are of the proper relative order of magnitude but are somewhat lower than the values obtained by other methods. This would indicate that the beginning of the absorption edge represents transitions to optical orbits rather than to infinity.

THE present work was undertaken in the attempt to increase the accuracy of the values of the outer energy levels of ten elements from antimony (51) to samarium (62) by photographing the L absorption spectra and emission lines of the same element that fell near the edge on the same plate. Thus, a direct measurement of the distance from the absorption edge to an emission line emitted when electron transitions take place between an N or an O level and the L level in question was made possible and promised to

afford a more accurate determination of these N and O levels than was to be expected when the calculations were based upon experimental data in which the emission lines have been measured by one investigator and the absorption limits by another.

Only one emission line was used for each edge, the $L\beta_2$ line for the L_{III} edge, $L\gamma_1$ for L_{II} , and $L\gamma_4$ for L_I . The difference in ν/R between the edge and the reference line in the three cases gave ν/R for the N_V level, the N_{IV} , and O_{II-III} respectively. It is apparent that small errors in the wave-length of the reference lines would not have an appreciable effect upon the computations involved in these outer levels. From the Bragg formula, a small difference, $\Delta\lambda$, is very approximately given by $\Delta\lambda = 2d\cos\theta\Delta\theta = (d/r)\cos\theta\Delta s$ where d is the grating constant, r the radius of the spectrograph, and Δs the distance on the plate between absorption edge and reference line. This last distance was never much more than 2 mm so that an error of two or three x-units in the reference line would have no appreciable effect upon the value of ν/R for the outer level under consideration. The angle $\Delta\theta$ corresponding to Δs , calculated from the plate measurements and subtracted from the angle θ for the reference line, gave us the angle θ corresponding to the edge with reference to the emission line. Other levels might have been determined in the same way but it was not apparent that the method would present any particular advantage unless the line fell close to the edge concerned. The elements used seemed of especial interest, as they represent an important region in the Periodic Table. It is worthy of mention that the L absorption limits obtained here for antimony, tellurium and iodine represent the *free* element and thus give the energy level values most characteristic of the element concerned.

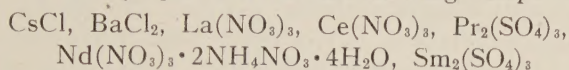
The L_I edge and the γ_4 line fall so close to each other that it was thought best to photograph them upon alternate horizontal portions of the same plate so that they would not be superposed. In some cases, they were photographed on separate plates together with a common reference line. It was also essential to remove all traces of the elements concerned from the target and focussing cylinder before making an L_I absorption edge, for traces of the γ_4 line might have been mistaken for this faint edge. It seemed conclusive that this had not occurred when the stronger $\gamma_{2,3}$ lines did not appear on the portion of the plate carrying the absorption. The exposures for the absorption edges were from two to four hours in length and for the emission lines from ten minutes for γ_1 or β_2 , to an hour for γ_4 .

DESCRIPTION OF APPARATUS

A Siegbahn precision vacuum spectrograph with a radius of approximately 18 cm was employed. The fore-pump used was a large two-stage oil pump. For the earlier part of the work, a Gaede molecular pump was used as a finishing pump and for the last part a mercury diffusion pump with liquid air. Transformers were used as the source of high potential with voltage regulation by means of rheostats in the primary circuits. The crystal was calcite.

PREPARATION OF THE ABSORBING SCREENS

As mentioned previously, the free elements were used in making the absorbing screens containing iodine, tellurium and antimony. Above xenon, the screens were prepared with the following compounds.



All of the salts used were soluble either in water or in an acid solution sufficiently dilute so that it did not destroy the paper of the absorbing screen. The screens were prepared by soaking a piece of paper in the solution and drying it rapidly over a Bunsen flame. In general, a satisfactory screen contained from 3 to 8 mg of the compound per cm^2 .

In the case of antimony, tellurium and iodine, the conditions for securing satisfactory absorption edges seem much more critical than is the case with the elements investigated above xenon and the increase in difficulty would appear to be too abrupt to be due merely to the increase in wave-length of the absorption edges. It is suggested that this may be at least partly due to the multi-valent nature of these elements. Coster has shown¹ that their different valence forms have L_{III} absorption edges differing from one another by one or two x-units. Moreover, it has been shown by one of the writers² that the x-ray beam may exert an appreciable reducing or oxidizing action upon a portion of the material in the absorbing screen. Thus, we could expect a superposition of the absorption edges of the different valence forms that would tend to reduce the sharpness of the main edge. The free element has the absorption edge of longest wave-length so that it would seem likely that the above difficulty would be minimized by using the free element to make the absorbing screen. Then, if secondary edges were produced because of change in valence of part of the material on the absorbing screen, they would fall on the short wave-length side of the main edge, i.e. in the region in which absorption is most marked and so would not have a tendency to obliterate the main edge by being partly superposed over it.

Some difficulty was experienced in producing screens containing the free element that were sufficiently thin and homogeneous to give satisfactory absorption since the usual method of soaking a paper in a solution of the substance was inapplicable. Tellurium was ground finely in an agate mortar and rubbed on paper in the dry state. For antimony, however, this method was not entirely satisfactory.

A very much finer form of metallic antimony was secured by a chemical precipitation. Hydrochloric acid was added to a water solution of potassium antimony tartrate until the precipitate first formed dissolved and a sheet of pure zinc was then placed in it. The zinc displaced the antimony from the solution of its salt and the latter collected as a very finely divided precipitate on the surface of the zinc. This precipitate was scraped off, washed repeatedly by decantation and filtered and in this way metallic antimony was

¹ Coster, *Zeits. f. Physik* **25**, 83 (1924).

² Chamberlain, *Phys. Rev.* **26**, 525 (1925).

secured having physical characteristics not unlike those of very finely powdered graphite. A very thin layer of this wet precipitate was spread over both sides of a piece of gold-beater's skin that had been previously weighed, and the whole was dried rapidly, after which it was weighed again and found to have about 1.5 mg of antimony per cm^2 . For the L_{III} edge, two layers, for the L_{II} edge four layers, and for the L_I edge six layers of the absorbing screen were used representing approximately 3, 6 and 9 mg of the metal per cm^2 respectively. With these screens satisfactory plates were obtained for all three absorption edges without difficulty.

A difficulty presented by free iodine is its tendency to sublime, for unless it is enclosed in an air-tight envelope, the iodine will all leave the absorbing screen in a very short time, particularly if it is in an extremely finely divided state. Iodine was precipitated by adding a water solution of potassium iodide to one of an excess of iodic acid and the precipitate of free iodine was washed, filtered, dried and spread in a very thin layer on gold-beater's skin. It was immediately sealed in an envelope of gold-beater's skin with collodion and kept in a desiccator in the presence of excess of iodine. This screen contained approximately 6 mg of iodine per cm^2 and the L_{III} edge was obtained with it without pumping out the spectrograph chamber.

It was apparent that a screen made by dissolving iodine in collodion would fulfill the condition of having the absorbing substance in an extremely finely divided state and could be used more satisfactorily in a vacuum. Iodine forms complexes, however, when dissolved in alcohol and if these were not destroyed when the alcohol in the collodion evaporated, the absorption edge might represent the compound instead of the free element. It seemed important that it should not do so, for slight variations in the wave-length of the absorption edge from this cause might produce a difference by no means negligible in the O_{II-III} energy level. A weighed amount of iodine was dissolved in alcohol in a small vial, about one cc of collodion added and the whole spread in a thin layer on the bottom of a glass dish after mixing thoroughly. The collodion film obtained contained approximately one-third mg of iodine per cm^2 and six layers were used for the absorbing screen. The film appeared light brown in color and perfectly homogeneous but it is essential not to dissolve too much iodine in a given amount of collodion or it will form crystalline patterns on the surface of the later with a consequent loss of homogeneity of the screen.

A comparison of the plates made of the L_{III} edge with the precipitated iodine screen and the collodion screen showed no appreciable shift of the absorption edge so it seemed safe to assume that any complexes formed by the alcohol were destroyed again or that the absorption edge of the complex did not differ appreciably from that of the free element. The collodion screen was therefore used for the remainder of the iodine edges and proved entirely satisfactory in a vacuum. The edges obtained, including L_I , were reasonably sharp and showed excellent contrast.

Table I contains the wave-lengths of the L absorption edges for free antimony, tellurium and iodine as computed from our measurements, together with the values of ν/R .

TABLE I

Wave-lengths of the L absorption edges for free antimony, tellurium and iodine.

Element	Absorption edge	Wave-length	ν/R	Reference line
51 Sb	L_I	2631.7 x-units	346.3	Sb $L\gamma_4$
	L_{II}	2821.9	322.9	Sb $L\gamma_1$
	L_{III}	2990.7	304.7	Sb $L\beta_2$
52 Te	L_I	2503.9	363.9	Te $L\gamma_4$
	L_{II}	2679.3	340.1	Te $L\gamma_1$
	L_{III}	2845.7	320.2	Te $L\beta_2$
53 I	L_I	2383.9	382.3	I $L\gamma_4$
	L_{II}	2547.5	357.7	I $L\gamma_1$
	L_{III}	2713.9	335.8	I $L\beta_2$

The values for the reference lines are taken from Coster's³ and Nishina's⁴ tables.

Table II gives the values of ν/R for the energy levels considered here.

TABLE II

Values of the energy levels, ν/R

	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Sm
N_{IV}	2.61	3.42	4.16	6.04	7.09	8.08	8.51	9.01	9.28	10.07
N_V	2.61	3.39	3.91	5.73	6.70	7.83	8.36	8.83	9.08	9.40
O_{II-III}	0.25	0.26	0.38	1.08	1.56	2.34	2.41	2.55	2.67	2.53

TABLE III

The square root of the values of the energy levels, $(\nu/R)^{1/2}$.

	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Sm
N_{IV}	1.62	1.85	2.04	2.46	2.66	2.84	2.92	3.00	3.05	3.17
N_V	1.62	1.84	1.98	2.39	2.59	2.80	2.89	2.98	3.01	3.07
O_{II-III}	0.50	0.51	0.62	1.04	1.25	1.53	1.55	1.60	1.63	1.59

TABLE IV

Energy levels in equivalent volts.

	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Sm
N_{IV}	35.4	46.3	56.3	81.8	96.0	109.4	115.3	122.0	125.7	136.4
N_V	35.3	45.9	53.0	77.6	90.7	106.1	113.2	119.6	123.0	127.3
O_{II-III}	3.4	3.5	5.2	14.6	21.1	31.8	32.6	34.5	36.2	34.3

DISCUSSION OF RESULTS

Figure 1 is a graph of the N_{IV} , N_V and O_{II-III} energy level diagrams obtained by plotting $(\nu/R)^{1/2}$ against the atomic number. Graphs obtained in this way are usually approximately straight lines that rise gradually with increasing atomic number. At the points at which electrons begin to be inserted again in groups previously in a state of temporary completion, the increase in energy is less because of shielding so that the level diagrams show a bend at the element before which this has occurred. Succeeding values lie in the new direction and the graph continues approximately linear. All three of our graphs are represented by two such portions that meet at lan-

³ Coster, Phil. Mag. **43**, 1070 (1922) and **44**, 546 (1922).

⁴ Nishina, Phil. Mag. **49**, 521 (1925).

thanum and the curves show a bend at that point. This is exactly what would be expected, for the next element, cerium, marks the beginning of the rare earth group and Bohr has stated that electrons begin to be inserted here in 4_4 orbits. This produces a distinct shielding effect upon these outer orbits so that they increase in energy less rapidly with increasing atomic number than previously, as is made apparent by a change of direction of the graphs and a distinct bend at the element before which the 4_4 group begins to receive electrons.

Since free elements were used in the absorbing screens for antimony, tellurium, and iodine, and compounds for the higher elements, this would

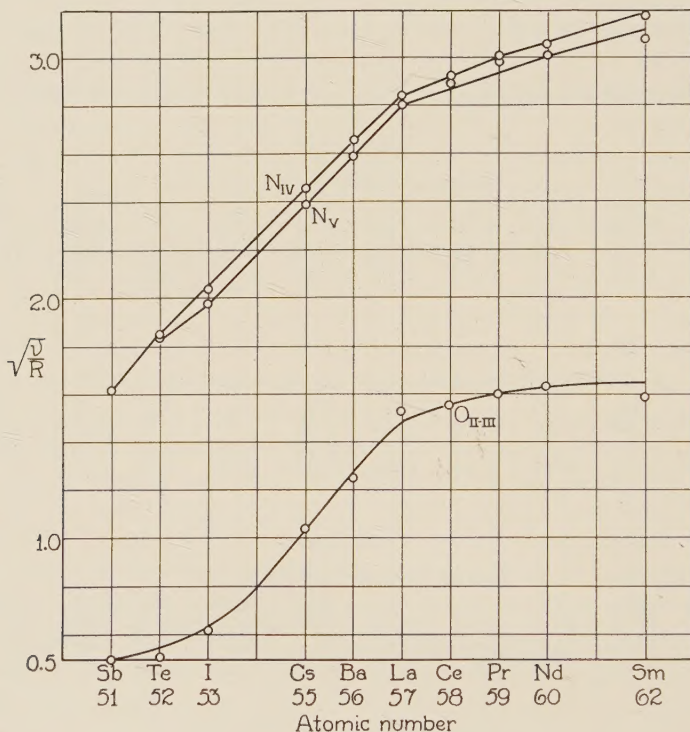


Fig. 1. Graph of the N_{IV} , N_V and O_{II-III} energy levels as functions of atomic number.

have a tendency to displace our energy level diagrams upward from caesium to samarium as the wave-length of the absorption edge with a compound is usually slightly less than with a free element. The only one of these elements whose absorption we have obtained in the free state is cerium and this shows little shift in the location of the absorption edges made with the free element as compared with those made with compounds, so it seems likely that the values of $(\nu/R)^{1/2}$ obtained here would be only slightly altered had it been practicable to use the free element in every case.

The O_{II-III} level is of particular interest because it represents the outermost occupied orbit in the case of antimony, tellurium and iodine and would

thus appear to offer direct experimental evidence of the precise meaning to be attached to absorption edge determinations such as these. Figure 2 is a diagram to represent the possible electron transitions that might be expected for these three elements. An electron ejected from the L_I orbit might go to infinity and a valency electron from O_{II-III} might drop back into the vacated place as is represented by *A* in the diagram. If this is the case, the energy difference in equivalent volts between the L_I edge and the γ_4 line should be equal to the ionizing potential. Another possibility is that the ejected electron from L_I can stop in the incompletely filled O_{II-III} level and an electron drop back from this same level to L_I giving rise to γ_4 radiation which would mean that the energy difference in equivalent volts between L_I and γ_4 would be zero. This is represented by *B* in Figure 2. The third possibility is that the electron ejected from L_I goes to a virtual orbit and one then drops back from O_{II-III} as is represented by *C* in the diagram.

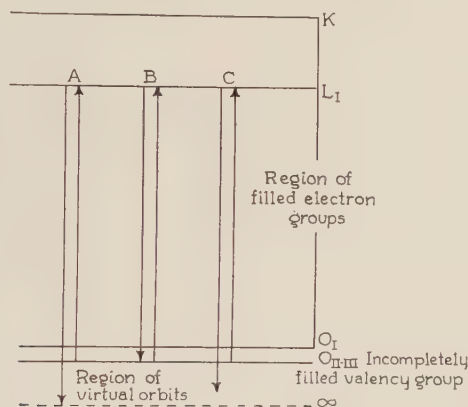


Fig. 2. Diagram to represent the possible electron transitions that might be expected in the case of antimony, tellurium and iodine.

In this case the energy difference in equivalent volts between the L_I edge and the γ_4 line would have a value somewhat less than the ionizing potential.

It will be noted that our values for O_{II-III} for antimony, tellurium and iodine are intermediate between zero and the ionizing potential. It will be realized that the actual separation of L_I and γ_4 in these cases is very small, smaller even than the correction applied for the half slit width. Moreover, these edges show a distinct gradient in blackening which raises a question regarding exactly which portion is to be considered the real beginning of the absorption. Our measurements were made by setting the microscope on the extreme limit of the blackest portion and then 0.05 mm was applied as a correction for the half slit width. Another difficulty is that γ_4 is an unresolved pair of lines and so not as narrow as could be desired.

For the reasons mentioned, it does not seem practicable to attempt to state too definitely the orbit to which transitions have occurred as indicated by the beginning of the absorption edge. It does seem possible, how-

ever, to state that the value of O_{II-III} obtained in this way cannot be as great as the ionizing potential, and to offer this as additional evidence that transition from inner orbits to virtual orbits do occur. Kossel,⁵ Coster and van der Tuuk,⁶ and Andrewes, Davies and Horton⁷ have also offered evidence of such transitions. This would apparently imply that all energy level determinations obtained as was done here represent the energy required to take an electron from the inner orbit concerned to infinity diminished by an appreciable fraction of the ionizing potential.

It might be noted that antimony, tellurium and iodine represent a particularly favorable group of elements in which to investigate the outermost occupied orbit. In the case of heavier elements K or L emission lines repre-

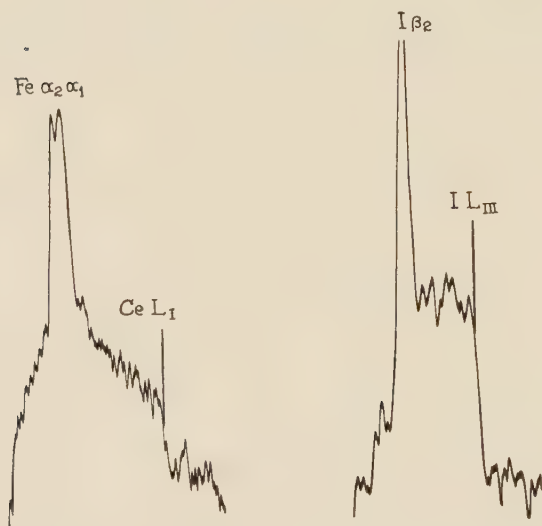


Fig. 3.

Fig. 3. Microphotometric records of absorption edges.

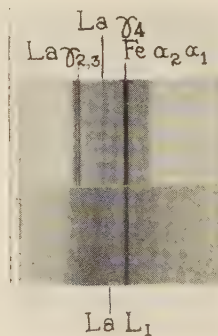


Fig. 4.

Fig. 4. Photograph of absorption edges.

senting the transition from the valency orbit are known for relatively few elements and similar investigations in the M series would represent much greater uncertainty and difficulty. In the case of lighter elements, experimental difficulties are increased by the necessity of dealing with longer wavelengths and by the increasing lack of sharpness of edges or lines representing transitions involving the valency ring.

Another interesting point is that the increase in ν/R from barium to lanthanum is as much as that from caesium to barium. The electron added at lanthanum is usually put back in a 5 quantum orbit while the two added just previously have gone into 6_1 . If this last added electron does go into a

⁵ Kossel, *Zeits. f. Physik* **1**, 119 (1920).

⁶ Coster and van der Tuuk, *Zeits. f. Physik* **37**, 367 (1926).

⁷ Andrewes, Davies and Horton, *Proc. Roy. Soc.* **A110**, 64 (1926).

5 quantum group, it might be expected to exert rather greater shielding than if it were added in a 6 quantum group and this would be made evident by a smaller increase in ν/R between barium and lanthanum than between caesium and barium. Beyond cerium, the O_{II-III} level runs horizontally within the limits of experimental error, as is to be expected in the case of elements representing the rare earth group.

Figures 3, 4 show photometric records and reproductions of certain absorption edges. As has usually been found with the free element on the absorbing screen, the iodine L_{III} edge shows a single discontinuity and no fine structure. The Ce L_I with cerium nitrate on the screen is of interest because it is unusually sharp for an L_I edge and gives evidence of the presence of a faint secondary edge on the short wave-length side of the main edge.

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